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Final Report (Part Two)

## ENCAPSULATED AEROSOLS

Prepared for:

U.S. ARMY CHEMICAL CORPS RESEARCH AND DEVELOPMENT COMMAND  
U.S. ARMY CHEMICAL WARFARE LABORATORIES  
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FINAL REPORT (PART TWO)

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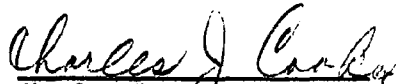
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## I SUMMARY

The final report for this work was written in two parts; the first part was issued April 17, 1961 and was entitled "Encapsulated Aerosols." The second part is presented here, and in conjunction with the 1961 report of the first year's work, is the complete final report.

All aerosol encapsulation methods studied during this investigation belong to one of three general approaches: condensation, coagulation, or indirect methods.

Encapsulation by condensation (using the core particles as condensation nuclei) proved to be a generally successful technique. This approach was extended to include methods in which vapor phase monomers were polymerized and condensed on the core particles. The polymerization reactions of diolefins, vinyl esters, and acrylate esters--promoted and catalysed by nitrogen dioxide vapors or boron trifluoride vapor--were investigated as a means of encapsulating phosphoric acid and dibutyl phosphite aerosol droplets. Vinyl acetate produced microcapsules with either boron trifluoride or nitrogen dioxide. Methyl acrylate produced microcapsules with boron trifluoride only. Under the conditions of these experiments, neither boron trifluoride nor nitrogen dioxide promoted sufficiently rapid polymerization of methyl methacrylate to produce microcapsules.

A two-stage microcapsule generator was designed to produce encapsulated aerosols. It consisted of two aspirator units in series. The aerosol generated in the first stage contained the core droplets. This aerosol was used to produce the second aerosol. The liquid droplets produced in the second aspirator stage tended to coalesce with and encapsulate the droplets from the first stage. Solutions of gelatin, cellulose nitrate, paraffin wax, polyethylene, and a natural rubber were used as encapsulation agents on phosphoric acid and phosphite esters. The capsule yields ranged from poor to excellent, depending upon the kind of solute and solvent used, the concentration of the solution, and the operating pressure in the system.



The microcapsule generator evolved through a number of design changes. The final unit was made of glass, Teflon, and polyethylene, and could be adjusted and disassembled. It produced 2-10  $\mu$  diameter capsules at relatively high generation rates.

Paraffin-encapsulated dibutyl phosphite was investigated to determine the effect of the paraffin film on evaporation rate under controlled conditions in dry and moist atmospheres. The evaporation rate of the capsule-core droplets was found to be considerably less than that of the bare-core droplets. Humidity produced little effect on the loss rate.

Simple spray drying of solutions of certain pairs of materials produced microcapsules in good yield. When dimethyl phosphite in polyethylene microcapsules were produced by spray drying a liquid dispersion of the two materials, both the relative concentration of the microcapsule components and the jet design were found to control the coat-to-core weight ratio.

The feasibility of generating microcapsules with extremely high inertial forces was investigated. A fluid energy mill, designed for grinding powders to micron-size particles, was utilized for this purpose. Attempts were made to prepare examples of all four phase pairs of microcapsules: liquid-on-liquid, liquid-on-solid, solid-on-liquid, and solid-on-solid. This approach was successful in the preparation of liquid-on-solid microcapsules. Liquid-on-liquid microcapsules could be made in fair yield. The solid-on-liquid combinations showed only a small fraction of encapsulation. One solid-solid pair from a mixed solid feed exhibited no true encapsulation, the product being a nearly homogeneous, finely ground (2-5  $\mu$ ) powder. A polymer solution and a solid powder feed, however, produced a small yield of polymer-encapsulated solid cores.

The ability of a process to form microcapsules is controlled by certain physical properties of the coating material-core material pair involved. Interfacial properties were considered to be generally important in this regard and the interfacial tensions of various liquid-solid and liquid-liquid pairs representing several types of encapsulated aerosols were measured.

A set of nine encapsulated aerosols, all of the combinations of three liquid cores (dibutyl phosphite, trioctyl phosphite, and phosphoric acid) and three polymer coats (paraffin wax, polyethylene, and rubber) were prepared in the two-stage generator, using core liquids in the first stage and toluene solutions of the polymers in the second stage. Values for the encapsulation efficiency for all of these microcapsules were determined. (Encapsulation efficiency is defined as the weight fraction of core material encapsulated.)

Spreading coefficients were determined for the nine pairs of core liquids and polymer films by measuring the height of drops of the liquids on prepared films of the solids under controlled conditions. The encapsulation efficiency of all of the systems in which polymer coatings were generated from solution was found to be proportional to the spreading coefficient. Spreading coefficient is a direct function of wettability.

A study was made of the encapsulation efficiency-wettability relationship in systems in which the cores were dibutyl phosphite and the polymer coatings were the binary mixtures, paraffin wax-polyethylene, paraffin wax-rubber, and polyethylene-rubber.

Encapsulation efficiency and wettability were found to depend on only one pure component or the other with sharp gradients at the transition concentrations. Because the encapsulated aerosols consisting of hydrophobic cores (phosphite esters) encased in polymer coats were of such great interest, much of the interfacial tension work was directed toward this class, even though direct interfacial tension measurements were impossible because of the miscibility of the core liquid and the polymer solvent. Direct liquid-liquid interfacial tensions were measured in the phosphoric acid-polymer film systems and in a phosphoric acid-oil film system. Encapsulation efficiency was found to be proportional to the product of the polymer solution concentration and the reciprocal of the liquid-liquid interfacial tension. The phosphite ester core-polymer coat microcapsules and the phosphoric acid core-polymer coat microcapsules exhibit the same kind of relationship between encapsulation

efficiency and spreading coefficient, and from this it may be inferred that the same properties control both kinds of microcapsules and that the mechanism of formation is the same for both.

Spreading coefficient is a direct, uncomplicated function of encapsulation efficiency in solid core-liquid film systems. The spreading coefficient of a series of solid core-film solutions systems were determined, and the weight fractions of core material encapsulation were also determined. For this class of pairs the encapsulation efficiency-interfacial tension relation was consistent with the relation discovered for liquid-liquid systems; i.e., the encapsulation efficiency was proportional to the product of the solution concentration and the negative reciprocal of the spreading coefficient.

## II INTRODUCTION

This study was made to investigate the basic principles involved in aerosol encapsulation. Microcapsules of all four combinations of liquids and solids, i.e., liquid-on-liquid, liquid-on-solid, solid-on-liquid, and solid-on-solid, were of interest. New techniques for the production of encapsulated aerosols were investigated. Methods were sought for the evaluation of the various approaches to aerosol encapsulation. The physical properties of the microcapsule core material-coating material pair were studied to determine which properties control in the various encapsulation processes. The particle size range of interest was from one to one hundred microns.

### III CONDENSATION POLYMERIZATION SYSTEMS

In an earlier phase of this work, reported in the first part of the Final Report, aerosol droplets were encapsulated by polymer films which were formed by rapid polymerization of vapor phase monomer. At that time, only diolefins with nitrogen dioxide were studied. In using nitrogen dioxide as a polymerization promoter, it is possible that some of the nitrogen dioxide could react with the core aerosol; however, the heterogeneous reaction rates are much slower than the gas phase reaction rates, and as the polymer film forms it tends to protect the core. In practice the core aerosol was mixed with the monomer mixture before exposure to the nitrogen dioxide. By selecting optimum mixing conditions and concentrations, exposure of the core material to nitrogen dioxide can be minimized.

Because of the success of nitrogen dioxide as a promoter in the polymer encapsulation of aerosol droplets, other possible types of rapid gas-phase polymerization reactions were sought.

Rapid polymerization of a number of monomers, in the gas phase, can be realized by the catalytic action of boron trifluoride. Three of the most reactive monomers were selected for study: methyl methacrylate, methyl acrylate, and vinyl acetate.<sup>1</sup> The fraction of core material encapsulated by the "polymerization-condensation" of these monomers using boron trifluoride catalyst was determined. Later, these same monomers were used with nitrogen dioxide replacing the boron trifluoride in a similar series of experiments. Details are described in the following paragraphs.

Phosphoric acid was selected as the core material in a series of experiments in which the encapsulation behavior of boron trifluoride-catalyzed polymerization was quantitatively compared with nitrogen

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<sup>1</sup>Burnett, G. M. Chemical Society Quarterly Review, 4, 306 (1950).

dioxide-promoted polymerization. Concentrations of core droplets, monomer, and promoter or catalyst were held constant in all experiments. A flow rate of 7 liters/min of nitrogen was used in the DeVilbiss nebulizer to generate the phosphoric acid aerosol. The appropriate monomer vapor was generated by passing nitrogen through the liquid monomer contained in a constant temperature bubbler (0°C). The nitrogen dioxide was generated in the same way. The flow rate of the boron trifluoride gas was measured by bubbling it through carbon tetrachloride. The bubble rate and bubble volume were determined and controlled to provide the desired rates. The monomer vapors and the promoter or catalyst concentrations were all approximately 500 ppm in the entire series of experiments.

Table I shows the percentage of core material encapsulated by the different polymer films as determined by phosphoric acid analyses made on pairs of collected products which were generated under identical conditions except that the reference runs on total acid were made with no promoter or catalyst.

Table I  
ENCAPSULATION OF PHOSPHORIC ACID DROPLETS  
BY CATALYST PROMOTED POLYMER FILMS

| Promoter          | Monomer       |                |                     |
|-------------------|---------------|----------------|---------------------|
|                   | Vinyl Acetate | Methylacrylate | Methyl Methacrylate |
| Boron trifluoride | 35%           | 40%            | None                |
| Nitrogen dioxide  | 35%           | None           | None                |

#### IV DETERMINATION OF WEIGHT FRACTIONS OF DIBUTYL PHOSPHITE ENCAPSULATED IN AEROSOL SYSTEMS

A procedure for the volumetric determination of dialkyl phosphites has been developed by Bernhart and Rattenburg<sup>2</sup> based on neutralization of the phosphite with excess sodium hydroxide (NaOH), then back titrating with hydrochloric acid (HCl). One mole of NaOH is consumed for each mole of dialkyl phosphite. By reducing solution concentrations and adjusting the volumes to accommodate small samples, the sensitivity of the method was increased one order of magnitude to about 0.1 micromole of dialkyl phosphite.

It was found that it was necessary to have about 150% excess of NaOH at a minimum concentration of 0.1N for quantitative phosphite neutralization. For a sample size up to 40  $\mu$ moles of phosphite, 1 ml 0.1N NaOH was adequate. The back titration was done with 0.01N HCl.

The weight fraction or weight percentage of core material encapsulated was selected as the quantitative function of encapsulation efficiency most generally measurable.

The encapsulated aerosol samples were collected for analysis first by gravitational settling on a glass slide and later with a low power impactor on a filter paper or directly on a glass fiber filter. An analytical procedure was developed for determining the percent encapsulation of dibutyl phosphite (DBP) droplets. Ten ml of ethyl alcohol were added to the collected aerosol sample; the mixture was stirred, then allowed to stand for a short time. Half of the alcohol was carefully decanted. The DBP content of the decanted portion was then determined directly. Five ml of heptane was added to the remaining sample aliquot. Upon thorough mixing, the heptane solvent released the encapsulated DBP, and the second half-sample was then analyzed for DBP. The amount of DBP found in the decanted sample subtracted from the amount in the residual sample was the amount encapsulated; this divided by the total DBP in the entire sample was the weight fraction encapsulated.

<sup>2</sup>Bernhart, D. N. and K. H. Rattenburg. Anal. Chem., 28, 1765 (1956).

This method could not be used when microcapsule films were encountered which were soluble in alcohol or water.

The decanted portion of the alcohol contained one-half of the unencapsulated DBP and no capsules. This was proven by the following experiments.

A split-stage collector, composed of two half circles of polyethylene, was arranged so that it rotated under a low force impactor. Each polyethylene semicircle received exactly half of a collected sample of encapsulated aerosol. One-half of the sample was then treated in the regular manner as described above. The remaining half sample was then treated in exactly the same manner, except that 5 ml of the heptane solvent for the encapsulating film was also added to the decanted part of the sample. If encapsulated phosphite were present, this decanted part would then show a phosphite content greater than the first decanted sample. No such difference was found, and the analytical procedure for DBP encapsulation was verified.

When the organic solvents were added to dissolve the encapsulating film, the combination of alcohol, solvent, and aqueous NaOH gave rise to a titration aberration. This solvent effect, slight in the case of the liquid paraffins, was proportional to the amount of 0.01N HCl required to back-titrate to the visual end point. For hexane or heptane solvent, using phenolphthalein indicator and the standard procedure with 1-ml NaOH, the blank correction (no DBP in sample) was 0.3 ml, which must be subtracted.

The correction was eliminated by the use of an improved indicator. This indicator was prepared<sup>3</sup> by dissolving 0.05 gm bromocresol green and 0.075 gm methyl red in 100 ml of 95% alcohol. With an acid titration, just after reaching an intermediate gray, the end point is a purple-red color. Basic titrations give a green end point after the intermediate gray.

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<sup>3</sup>Goldenson, J. and J. W. Thomas. J. Ind. Hyg. Tox., 29, 14 (1947).



## V DEVELOPMENT OF THE TWO-STAGE MICROCAPSULE GENERATOR

### A. First Systems Investigated

Under ideal conditions two immiscible liquids can be mixed and atomized using a gas under pressure in an ordinary two-fluid nozzle to produce a large fraction of two-phase droplets, with one liquid phase encapsulating the other. This approach was used with some success when applied to mixtures of phosphoric acid and tung oil earlier in this work. When these two-phase droplets were exposed to nitrogen dioxide to polymerize the tung oil, 30% of the phosphoric acid was found to be encapsulated.

Mixing the two bulk liquids severely limits the number of possible pairs. They must be immiscible, they must have no tendency to react chemically, and the emulsion viscosity must not be too great. DBP and aqueous gelatin solution (3% gelatin by weight) were mixed and nebulized together as a classic example of an immiscible system. The droplets were collected and microscopically examined. Figure 1 is a photomicrograph of some of the large capsules which were formed.

Encapsulation was shown qualitatively by comparing weight changes of core material in unencapsulated samples and encapsulated samples, both stored for the same length of time under identical conditions. (Because of the solubility of gelatin in aqueous systems the quantitative determination of the weight fraction of DBP encapsulated would have been difficult.) To obtain this comparison two pairs of duplicate samples, one pair unencapsulated, the other pair encapsulated, were analyzed for DBP by titration; one sample of each pair was analyzed immediately, the other sample of each pair was analyzed after exposure. After 65 hours' dark-room exposure to clean filtered air at ambient temperature and humidity, the bare DBP droplets lost 61% of their weight while the weight loss of the gelatin-encapsulated droplets was 52%.



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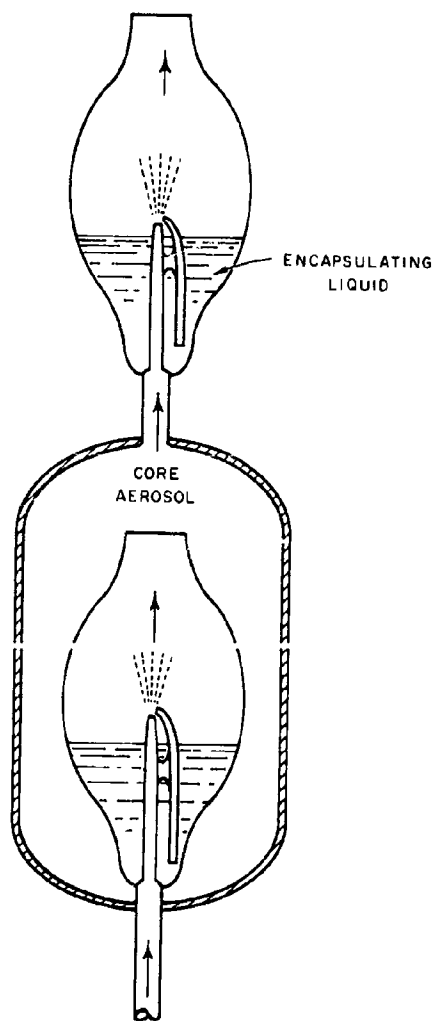
FIG. 1 DIBUTYL PHOSPHITE DROPLETS ENCAPSULATED IN GELATIN

Although earlier experiments with Venturi mixers and high velocity mixing tubes showed that these devices were not efficient promoters of aerosol encapsulation, a two-stage aerosol generator, with two aspirator jets in series was felt to be capable of producing relatively large forces in its jet nozzles at moderate pressure drops. De Vilbiss nebulizers were first used for the two jets. The first-stage nebulizer, containing the core droplet material, was encased in a pressure chamber. The aerosol produced by the first stage was used to aerosolize the encapsulating liquid in the second-stage nebulizer. The second stage jet of the generator was operated at sonic velocity (critical flow) to provide large inertial forces between the aerosol containing the core droplets and the "encapsulating" droplets being generated. A diagram of the first generator design is shown in Fig. 2.

The encapsulating ability of three polymer solutions in the second stage of the microcapsule generator was investigated with DBP in the first stage. The first solution was 1% polyethylene in toluene. No direct titrations were made, but collected samples were given the storage weight-loss tests. In 16 hours the blank sample lost 25% of its weight of DBP. The encapsulated sample did not lose any weight.

The second encapsulating solution was 5% cellulose nitrate in acetone. The percent DBP encapsulated was determined by the standard procedure, except that acetone was used to dissolve the cellulose nitrate films. Forty-eight percent of the DBP was encapsulated.

Natural rubber in carbon disulfide was the third encapsulating solution. The concentrations used were about one percent by weight rubber. Capsules were observed using the phase contrast microscope; they released liquid when they were scraped together and crushed. Hydrolysis of carbon disulfide solvent interfered with the quantitative determination of encapsulation.



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FIG. 2 TWO-STAGE MICROCAPSULE GENERATOR

B. Some Problems Encountered in Developing the Microcapsule Generator

Liquid core-solid coat microcapsules are important as a class. It may be desirable in many applications to encase liquid droplets in a solid envelope. Solutions of these encapsulating solids can be used in the second stage of the two-stage aspirator generator; however, there are a number of limiting factors and conditions which restrict the scope of application of this approach. One difficulty encountered with the early generator design was its inability to produce phosphoric acid cores in good yield because of excessive coagulation of the droplets of phosphoric acid in the jet of the second stage aspirator.

Three rubber solutions were used in attempts to encapsulate phosphoric acid with rubber; the solvents used were carbon disulfide, a mixture of one part carbon disulfide plus nine parts carbon tetrachloride, and a mixture of one part carbon disulfide plus nine parts n-heptane. These experiments were difficult to evaluate because of the poor generation rate of phosphoric acid aerosol droplets.

Solvent evaporation tended to limit the generator operation to short periods because of thickening of the encapsulating solution when volatile solvents were used in the second stage. In an attempt to improve operation the carrier gas was precooled to decrease solvent evaporation. A copper coil was added to the nitrogen line immediately ahead of the generator, and the coil was immersed in an isopropanol-dry ice bath. The precooling was partially successful, but it was not the final answer to the problem. Evaporation of solvent continued to interfere with generator operation in the systems utilizing volatile solvents.

The next approach in the use of liquid encapsulating materials involved the preparation of solvents with low vapor pressures at room temperature and melting points above room temperature. The melting points of solutions of commercial paraffin wax in many liquid paraffins were determined and solid wax solutions were compared with respect to firmness at room temperature. The best combination noted was 17% by weight paraffin wax in dodecane. This solution melted at 55°C and produced a hard wax at 25°C.

The generator was operated with the second stage aspirator heated to 80°C with an external heating tape. Using DBP in the first stage and with a supply gas pressure of 25 psig (total flow of about 15 liters N<sub>2</sub> per minute) microencapsulation of DBP in paraffin was accomplished in excellent quality and yield.

Typical results using the wax-dodecane mixture are presented in Table II.

Table II  
PARAFFIN WAX MICROENCAPSULATION OF DIBUTYL PHOSPHITE

| Run No. | Operating Time (min) | DBP Encapsulated (wt percent) | Production rate (mg DBP/min) |
|---------|----------------------|-------------------------------|------------------------------|
| 1       | 2.0                  | 98.9                          | 8.7                          |
| 2       | 2.0                  | 94.7                          | 7.6                          |
| 3       | 1.0                  | 85.0                          | 7.6                          |

The two-stage microcapsule generator was again modified by adding a solvent make-up unit which was designed to continuously replace the solvent lost by evaporation in the second stage aspirator by means of gravity flow of solvent from a reservoir into the aspirator. The flow rate of make-up solvent was controlled by adjusting the hydraulic head and was regulated to maintain the liquid level in the aspirator. The generator with the second stage solvent reservoir is shown at the upper right in Fig. 3.

With the generator capable of handling volatile solvents while operating at room temperature, three different microcapsules were produced. Hexane was the solvent used for paraffin wax and rubber, and toluene was the solvent used for polyethylene. DBP was the material encapsulated in each case. The collected material was examined under a phase contrast microscope. In addition to unencapsulated DBP droplets and solid film particles, a third kind of particles, which were most probably the microcapsules of DBP in rubber, was observed on all three slides.

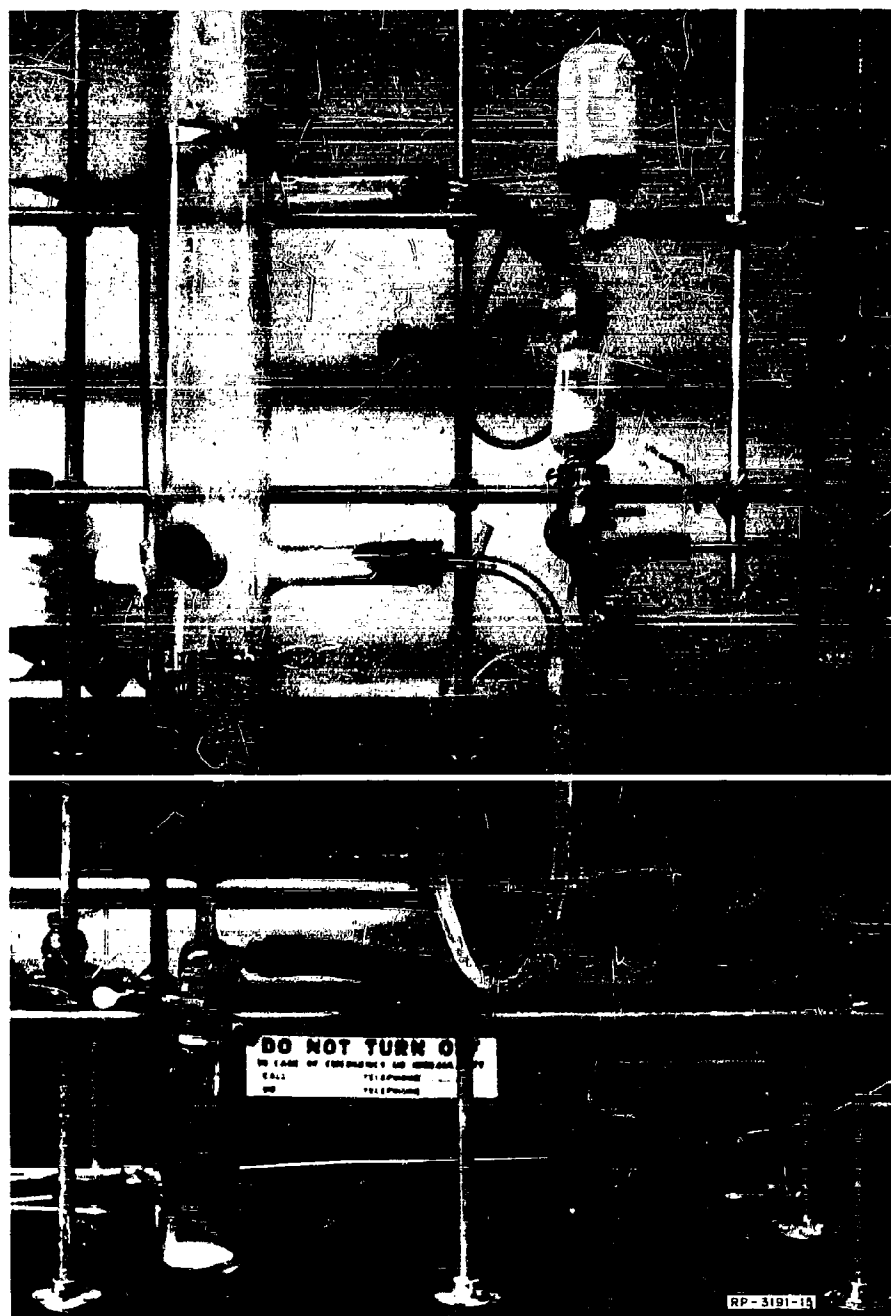


FIG. 3 TWO-STAGE MICROCAPSULE GENERATOR WITH MICROCAPSULE COLLECTOR

A modified unit was developed for collecting these capsule preparations. The revised collector was a low-powered impactor (shown at the bottom in Fig. 3). This unit improved collection efficiency without subjecting the microcapsules to mechanical forces so strong that the microcapsules would be smashed upon impaction.

C. The Effect of Solution Concentration on Solid-on-Liquid Microcapsule Production

The two-stage aspirator generator proved to be generally useful for the production of liquid-on-liquid and solid-on-liquid aerosols. When a solid coating was desired, usually a solution of the encapsulating solid was made in a volatile solvent. This method of generating solid-on-liquid aerosols was sensitive to several factors including solvent type and solution concentration. The effect of solution concentration on generator performance was investigated using DBP in paraffin wax with n-hexane as the solvent. Encapsulation runs were made using 5% and 10% by weight paraffin wax in n-hexane. When a 20% paraffin wax solution was added to the aspirator reservoir, it was found to be too viscous to produce an aerosol.

The results of these encapsulation experiments are presented in Table III.

Table III  
ENCAPSULATION EFFICIENCY OF PARAFFIN WAX FROM  
HEXANE SOLVENT ON DIBUTYL PHOSPHITE

| Paraffin<br>in Hexane<br>(wt percent) | Coat-Core<br>Ratio          | Encapsulation<br>(wt percent) |
|---------------------------------------|-----------------------------|-------------------------------|
| 5.0                                   | 1.5/1                       | 15                            |
| 5.0                                   | 1/1                         | 15                            |
| 10.0                                  | 3/1                         | 43                            |
| 10.0                                  | 3/1                         | 37                            |
| 20.0                                  | Too viscous to form aerosol |                               |



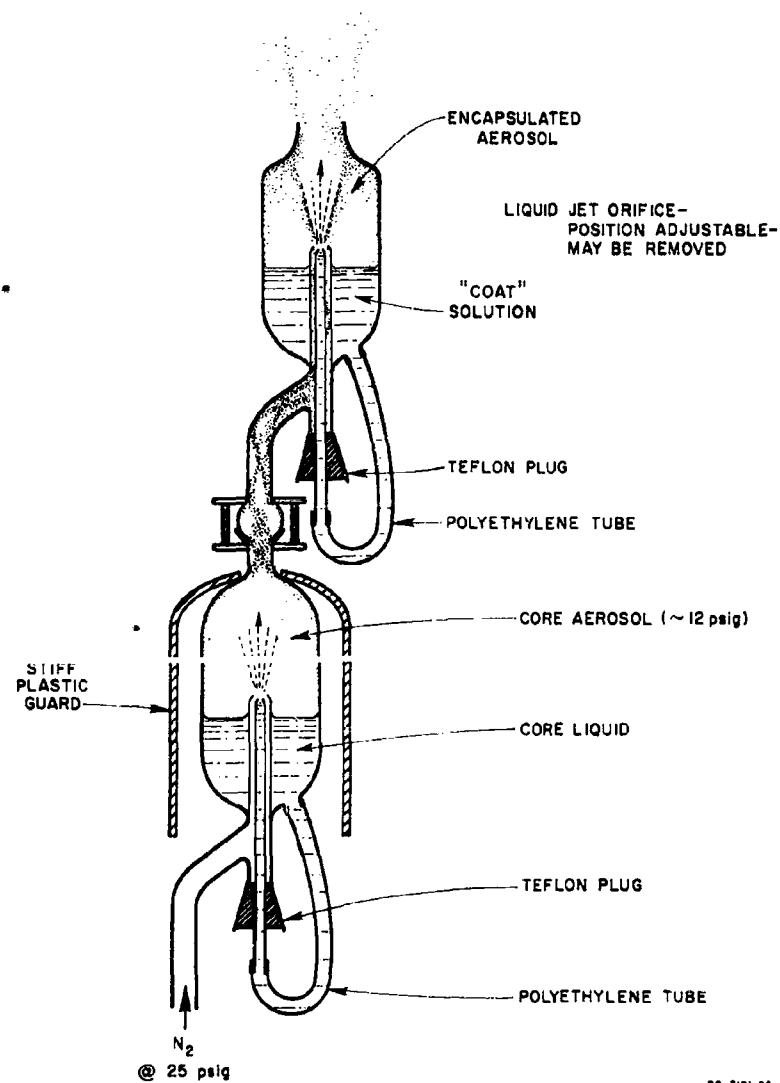
#### D. Other Generator Designs

The De Vilbiss nebulizers, when used as aspirators in the two-stage generator, were difficult to open when they became plugged. Their aerosol production rate was small. In an attempt to eliminate these problems, three different generators were designed, fabricated, and tested.

Design number two was all glass, with larger dimensions and an increased generating capacity, but it, too, was difficult to clean.

A third generator was constructed of metal, with brass aspirators and an aluminum body. This unit produced encapsulated aerosols with non-corrosive liquids.

Finally, based on the experience gained in operating the earlier designs, a glass, Teflon, and polyethylene generator was evolved which eliminated the disadvantages of the earlier models. This generator is illustrated in Fig. 4. The generator was operated with a total pressure drop of 25 psi across both jets. The jet positions were adjustable, and if clogging occurred, the jet tubes were removable for easy cleaning.



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FIG. 4 FINAL DESIGN OF THE TWO-STAGE MICROCAPSULE GENERATOR

## VI EVAPORATION RATES OF MICROCAPSULES

Paraffin wax-encapsulated DBP was exposed to an atmosphere of nitrogen at three relative humidities and the rate of loss of DBP from the microcapsules was compared with the rate of loss from unencapsulated DBP aerosol droplets generated in the same manner under the three conditions. The Plexiglas chamber in which the exposures were made is shown in Figure 5, and Figure 6 is a flow diagram of the system. The effect of encapsulation and the lack of effect of water vapor are shown in Table IV.

Although only one series of experiments was done, the value of the procedure for determining the effect of encapsulating droplets or particles on their evaporation rates, was demonstrated.

Table IV

COMPARISON OF EXPOSURE LOSSES BETWEEN MICROCAPSULES  
AND BARE LIQUID CORES

| Type Exposure (T=25°C)       | Linear Gas Velocity Over Sample (cm/sec) | Exposure Time (hrs) | DBP Encapsulated in Capsule Sample (wt percent) | Loss of DBP in Capsule Sample (wt percent) | Loss of DBP Droplet Sample (wt percent) |
|------------------------------|--|---------------------|---|--|---|
| Dry N <sub>2</sub>           | 0.7                                      | 1.5                 | 53  | 0  | 35                                      |
| Dry N <sub>2</sub>           | 0.7                                      | 1.5                 | 62  | 0  | 32                                      |
| Dry N <sub>2</sub>           | 0.7                                      | 3                   | 20  | 30*  | 47**                                    |
| Wet N <sub>2</sub><br>50% RH | 1.4                                      | 3                   | 13  | 28*  |   |
| Wet N <sub>2</sub><br>80% RH | 0.7                                      | 3                   | 48  | 18   | 47                                      |

\*Probably due to large fraction unencapsulated.

\*\*Assumed to be the same as for wet N<sub>2</sub>, 80% RH.

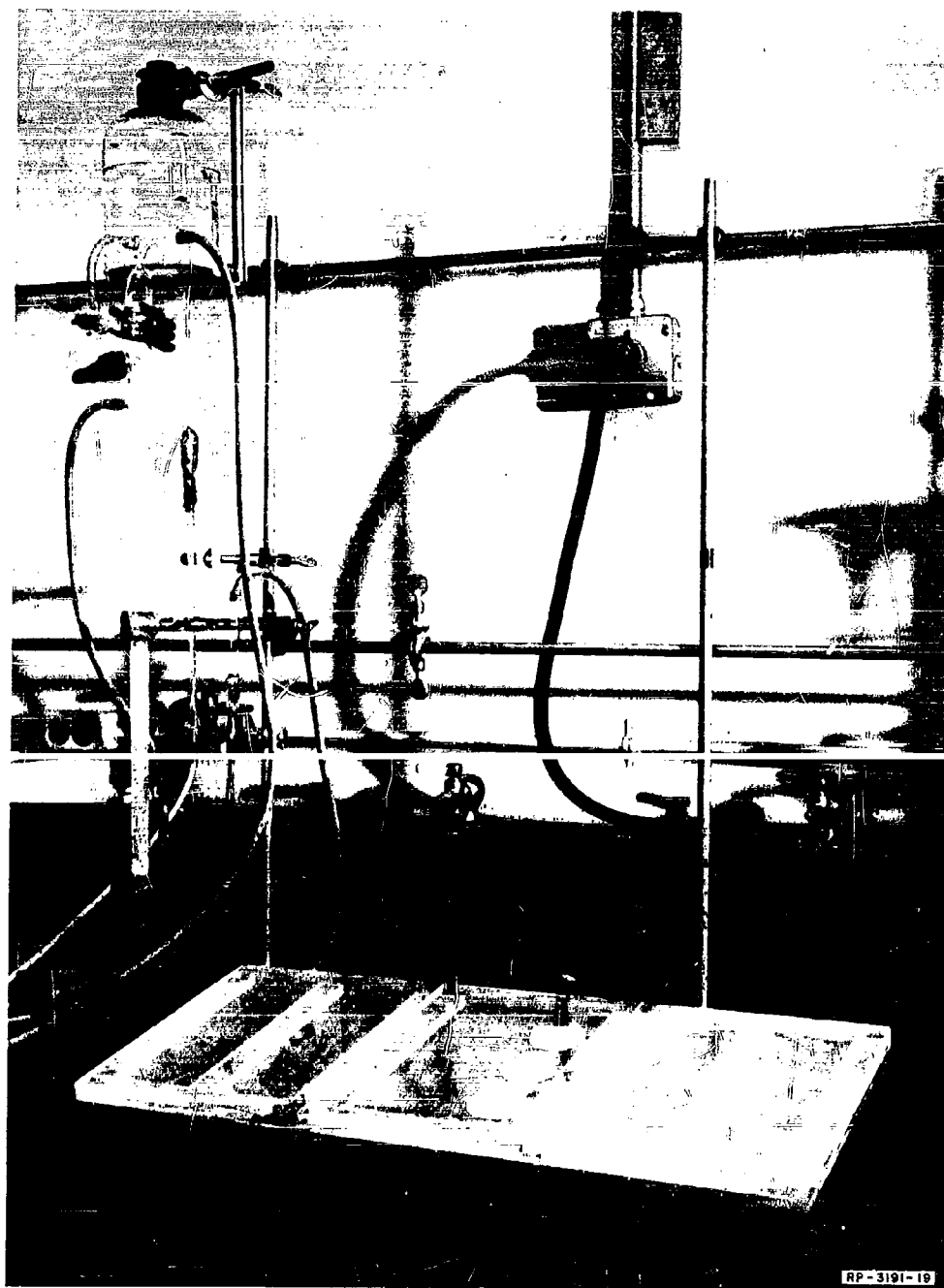


FIG. 5 CONTROLLED EVAPORATION RATE APPARATUS

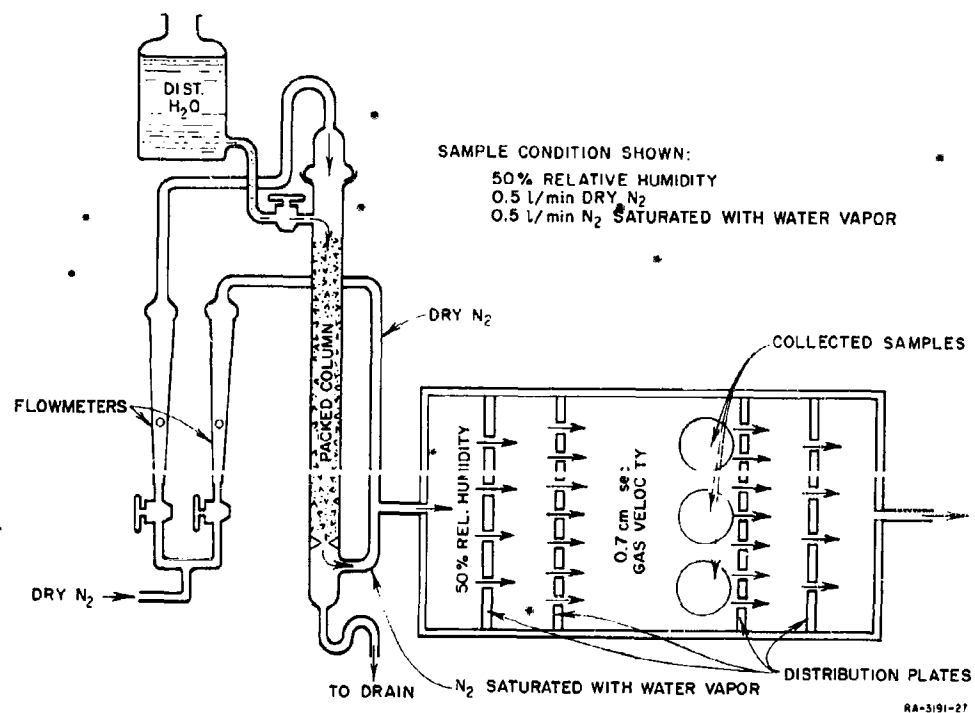


FIG. 6 CONTROLLED EVAPORATION RATE SYSTEM SHOWING HUMIDIFIER DETAILS

## VII MICROCAPSULES PRODUCED BY SPRAY DRYING

Dimethyl phosphite was encapsulated in low molecular weight polyethylene by mixing dimethyl phosphite and a polyethylene solution in a single-stage aspirator and spraying the mixture into a current of warm air. With a De Vilbiss paint spray gun, when the polyethylene concentration was 10%, the coat-core weight ratio of the capsules was 1.5 to 1. With a different type nozzle, a 5% concentration of polyethylene produced a coat to core ratio which was larger than 1.5 to 1.

It was shown in Part One of the Final Report (report on the first year's work) that this was an effective method for producing microcapsules.

## VIII THE FLUID ENERGY MILL AS A MICROCAPSULE GENERATOR

Fluid energy mills have been used to a limited extent for coating powders, and claims have been made that they could be used for the production of microcapsules.\* We have investigated the ability of a 4-inch Jet Pulverizer to produce microcapsules of the four phase combinations.

The procedures were similar for all four combinations. The mill was operated with compressed air at 100 psig in the ring manifold. If this size Jet Pulverizer is to be used for the grinding of powders, a normal feed rate is 100 to 200 grams per minute. For convenience, we operated at feed rates of about 5 to 10 grams per minute with both solids and liquids. All of the material was fed into the normal feed inlet.

When two liquids were used, they were fed as separate streams from burettes or glass tubes into the opening. When a liquid and a solid were used, they also were fed as separate streams, but in the case of two solids the material was premixed and then fed in the normal manner.

The samples were collected in a jar under the grinding chamber. The results of the attempted formation of the different kinds of microcapsules are summarized in the following paragraphs.

Liquid-on-liquid: Mineral oil (pure white paraffin oil) and 86% ortho-phosphoric acid were fed into the mill. When equal volumes were fed, some encapsulation of the acid by mineral oil occurred. With a 3:1 or 4:1 volume excess of mineral oil, nearly all of the phosphoric acid droplets appeared to be encased in oil upon microscopic examination.

Liquid-on-solid: Mineral oil and oxalic acid were used. At a coat to core ratio of 1:1, microscopic examination showed encapsulation to be virtually complete. Of the four phase combinations, microencapsulation of solid cores by liquid coats is generally the easiest to accomplish.

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\*Advertising chains of Jet Pulverizer Company, Palmyra, N.J., and Sturtevant Mill Company, Boston, Mass.

While examination revealed that discrete capsules were formed in the fluid energy mill, it would be necessary to utilize them as they emerged if an encapsulated aerosol were desired. After collection and agglomeration, it would be extremely difficult, if not impossible, to redisperse these liquid-on-solid microcapsules in an aerosol. The same limitation would apply to the liquid-on-liquid microcapsules.

Solid-on-liquid: Because of the great interest in this phase combination, three of these pairs were studied. Paraffin wax in toluene solution, and DBP were fed into the mill. A number of runs were made using different coat to core ratios. All of the material collected had 8% encapsulation by phosphite analysis. Next, paraffin wax in toluene solution and phosphoric acid were used; and last, polyethylene in toluene solution and phosphoric acid were tried. Neither of the last two combinations produced encapsulation in the fluid energy mill treatment.

Solid-on-solid: Paraffin wax in toluene solution and oxalic acid were fed into the mill in separate streams. Eight percent of the oxalic acid in the collected aerosol was encapsulated, as determined by analysis. A second solid-on-solid pair, sulfur and oxalic acid, was mixed and fed into the mill. This combination did not show any true encapsulation, but the treated material was an intimately mixed, homogeneous powder, ground to 2 to 5 micron particle size.



## IX MICROCAPSULE SAMPLES PREPARED FOR CHEMICAL WARFARE LABORATORIES

Two samples of microcapsules were prepared for examination by Chemical Warfare Laboratories. There were (1) dibutylphosphite (DBP) coated with Zytel (a nylon resin) and (2) dimethyl phosphite (DMP) coated with polyethylene (PE).

The DBP was encapsulated by Zytel in the two-stage generator. In the first attempts to prepare the DBP in Zytel capsules, the Zytel solvent was a mixture of five parts ethanol, four parts toluene, and one part cellosolve. The product was a wet paste which had retained the nonvolatile fraction of the Zytel solvent. The solvent was changed to pure ethanol and a 3% solution was used. The product, which was collected electrostatically, was a dry powder. Analyses of the capsules showed 20% by weight DBP.

The second sample, DMP capsules, was prepared by spray drying of toluene solution of DMP and PE. They were incorporated into the solution at a 1:1 ratio of PE to DMP. The microcapsules were isolated by spray drying in warm air. Analyses of the capsules showed 30% by weight DMP. Before shipment, microscopic examination revealed that liquid was liberated upon crushing the DMP in PE microcapsules.

The two samples were sent to the Chemical Warfare Laboratories, and there the DMP capsules were analyzed; first for phosphite content which showed less than 2% by weight DMP. A second analysis for elemental phosphorus showed 31% by weight as DMP. In addition to the chemical analyses, microscopic examinations of both the DBP and DMP capsules were made after crushing. No free liquid was observed in either sample. Obviously, under normal handling conditions, hydrolysis of these microcapsules was not retarded to any great extent.

## X PHYSICAL PROPERTIES AND ENCAPSULATION EFFICIENCY

Microcapsules composed of liquid cores covered by continuous solid films have the most important application potential of the various possible kinds of encapsulated aerosols. We have shown that the best general method for producing this type of microcapsule is via the two-stage generator using a solution of the film material in a volatile solvent in the second stage. Thus, the encapsulating material originates as a liquid film which then undergoes a change to a solid film. Unfortunately from the point of view of understanding these encapsulation processes, most of the polymer solvents are necessarily organic liquids and most of the core liquids (e.g., phosphite esters) will be miscible with these organic solvents. Determining the properties controlling encapsulation in such systems is difficult because of the inherent complexity of the encapsulation mechanism. Regardless of the mechanism, the solid material does eventually form a continuous film on the surface of the core liquid and the encapsulation tendency must have a relationship to the wettability of the film by the liquid. Because organic phosphites were of great interest as candidates for aerosol encapsulation, DBP was selected as the core liquid and three film-forming substances, paraffin wax, low molecular weight polyethylene, and natural rubber, were chosen for encapsulating materials. All of these polymers were dissolved in toluene. The paraffin wax and the rubber solutions in toluene were 5% by weight solute, but it was found to be impossible to work with 5% by weight polyethylene solution.\* A 1.4% by weight polyethylene solution was used throughout the evaluation of physical properties.

Spreading coefficient,  $Sc$ , is defined as the energy released per unit area when a liquid spreads over a substrate. The spreading coefficient, is made up of three components which are the surface energies of the three interfaces involved. In the case of a liquid on a solid they are the solid-gas interfacial energy,  $\pi_s$ , the liquid-gas interfacial

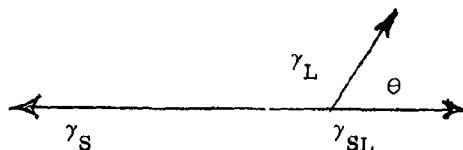
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\*The solution was unstable and became cloudy upon standing.

energy,  $\pi_L$  (this term is directly related to and numerically equal to the surface tension of the liquid), and the solid-liquid interfacial energy,  $\pi_{SL}$ , in the following relationship:

$$Sc = \pi_S - \pi_L - \pi_{SL} .$$

The spreading coefficient can be obtained indirectly by measuring the liquid surface tension,  $\gamma_L$ , and the contact angle  $\theta$  of the liquid with the solid. At equilibrium, the forces acting at the boundary of the interfaces must balance:



$$\gamma_S - \gamma_{SL} - \gamma_L^* \cos \theta = 0 .$$

As the interfacial energies and interfacial tensions can be equated, it follows then that

$$Sc = \gamma_L (\cos \theta - 1)$$

and values for  $Sc$  in a solid-liquid system can range from 0, with complete wetting of a solid by a liquid, to  $-2\gamma_L$ , at the opposite extreme where no wetting occurs at all. If we keep in mind the negative sign of  $Sc$  values we find that  $Sc$  and wettability are direct functions.

Padday<sup>4</sup> has developed a method for determining the spreading coefficient by measuring the height of a drop of the liquid on the horizontal solid surface. He showed that the quantitative relationship between spreading coefficient and drop height in the case of a liquid on a solid must be:

$$Sc = - 1/2 \rho g h^2$$

<sup>4</sup>Padday, J. F. A New Method for Measuring the Spreading Coefficient of a Liquid on a Solid Surface, Proc. of the 2nd Data Congress of Surface Activity, Vol. III, 136, Butterworths (1957)

where

$\rho$  is the density of the liquid,

$g$  is the gravitational constant,

and

$h$  is the equilibrium drop height.

The derivation was based on relating the surface energy with the potential energy of a drop which has a sufficiently large radius compared with its height to assure equilibrium conditions in the drop.

We used Padday's approach in determining spreading coefficients of liquids on solid. The experimental details of the procedure used are described in the Appendix.

It was necessary to develop a method for producing solid films which would be representative and repeatable. In encapsulation with the two-stage aspirator generator the capsule films are formed by solvent evaporation; therefore, the films for spreading coefficient measurements were also made by solvent evaporation. This was done by spreading layers of solution on glass slides and allowing the solvent to evaporate in a gentle air stream at room temperature. Successive applications of the solution were made and permitted to dry until the solid films were thick enough to give reproducible spreading coefficient values. These films were 200 to 500 microns thick.

First, the effects of temperature, humidity, film age, and film roughness on the spreading coefficient were evaluated.

Investigation of the temperature effect between 18°C and 25°C showed that the negative value of the spreading coefficient increased with temperature, i.e., wettability decreased with increasing temperature.

Humidity studies were carried out with the aid of constant humidity chambers and humidity-controlled flow systems. After the films were manufactured they were aged in constant humidity environments at 0, 50, and

100 percent humidity. The 50% relative humidity environment was maintained by having a saturated calcium nitrate solution in water vapor-solution equilibrium with the air space above it.

During the drop-height measurements, atmospheres of the correct humidity were generated continuously and these gases were passed slowly through a transparent plastic box enclosing the film and drop. Relative humidity effects were consistent in all three films, with wettability of dibutyl phosphite increasing with increasing humidity (decreasing negative value of  $Sc$ ).

Wettability of the films also tended to increase with increasing film age. Conversely, increasing roughness caused a decrease in wettability.

Temperature and relative humidity coefficients and changes of  $Sc$  when the film aged from one to two days were calculated. As it was necessary to permit the films to age somewhat, films 24 hours old were selected as being adequately stable. The films were examined visually after preparation. Any malformed or rough films were discarded.

The  $Sc$  values and the effects of changing conditions are presented in Table V.

Table V

SPREADING COEFFICIENTS OF DIBUTYL PHOSPHITE ON SOLID FILMS  
WITH TEMPERATURE AND RELATIVE HUMIDITY COEFFICIENTS  
AND FILM AGING EFFECT

|              | $Sc^*$<br>(dynes/cm <sup>2</sup> ) | Temp Coeff.<br>$\Delta Sc/^\circ C$ | RH Coeff.<br>$\Delta Sc/\%RH$ | Change in<br>$Sc$ Between<br>Film Ages of<br>24 and 48 hours<br>(dynes/cm <sup>2</sup> ) |
|--------------|------------------------------------|-------------------------------------|-------------------------------|--|
| Paraffin wax | -3.1                               | -0.2                                | .024                          | 0.5  |
| Polyethylene | -0.10                              | -0.01                               | .0006                         | 0.02   |
| Rubber       | -4.2                               | -0.3                                | .008                          | 1.5  |

\* Reference conditions: 25°C, 0% relative humidity films aged 24 hrs at 0% RH.

Three encapsulated aerosols, using DBP cores with the three film materials were then produced with the microcapsule generator. They were collected and the weight fraction of encapsulated DBP was determined. Then spreading coefficients of DBP on the three films were measured under conditions which were selected as standard, i.e., 25°C and 0% relative humidity.

The spreading coefficient of DBP on polyethylene is a very small negative number, much smaller than the spreading coefficient of DBP on paraffin wax which, in turn, is not as large a negative number as the spreading coefficient of DBP on rubber. The order of decreasing wettability in the three films is polyethylene, paraffin wax, rubber. The results of the encapsulation efficiency measurements show that encapsulation efficiency increases as the wettability of these films by the liquid core materials decreases.

Phosphoric acid and trioctyl phosphite liquid cores were also used. The three liquids in combination with the three film materials yielded nine microcapsule pairs for study. Encapsulation efficiencies and spreading coefficients were determined for each pair.

The data are presented in Table VI. In Figure 7 the increasing encapsulation efficiency with decreasing wettability relation is shown to be true for all nine of these pairs.

The spreading coefficient values for the three DBP pairs ranged from -0.10 erg/cm<sup>2</sup> for the polyethylene film to -4.2 ergs/cm<sup>2</sup> for the rubber film. Films of intermediate composition (binary mixtures of the film materials) were next studied, against the possibility that the encapsulation efficiency-spreading coefficient relation of these film mixtures with DBP would help explain the encapsulation processes involved. Systems containing the three binary films, paraffin wax-polyethylene, paraffin wax-rubber, and polyethylene-rubber, were investigated in detail. In addition to spreading coefficient and weight percent DBP encapsulated, the viscosities of the film solutions in toluene at 25°C and the solution

Table VI

RELATION BETWEEN ENCAPSULATION EFFICIENCY  
AND SPREADING COEFFICIENT

| Liquid             | Film         | Encapsulation<br>(wt percent) | Spreading<br>Coeff.<br>(ergs/cm <sup>2</sup> ) |
|--------------------|--------------|-------------------------------|--|
| Dibutyl phosphite  | Polyethylene | 11                            | -0.10  |
|                    | Paraffin     | 21                            | -3.1   |
|                    | Rubber       | 33                            | -4.2   |
| Trioctyl phosphite | Polyethylene | 2                             | -0.14  |
|                    | Paraffin     | 8                             | -1.5   |
|                    | Rubber       | 23                            | -8.5   |
| Phosphoric Acid    | Polyethylene | 14                            | -1.3   |
|                    | Paraffin     | 26                            | -19.8  |
|                    | Rubber       | 39                            | -29.8  |

densities were determined. These data are presented in Tables VII, VIII, and IX and the spreading coefficient-encapsulation efficiency data are summarized in Figure 8.

A critical examination of the data from these three tables reveals that in two of the binary systems both spreading coefficient and encapsulation efficiency are controlled only by one component or the other exclusively, with sharp region of change-over of control in the binary composition.

In Table VII, paraffin wax-polyethylene, the transition composition is 24% by weight paraffin. In Table IX, polyethylene-rubber, the transition composition is 1% polyethylene, i.e., in this binary, polyethylene alone controls the encapsulation efficiency and spreading coefficient over 99% of the composition range. The differences in the paraffin wax-rubber binary (Table VIII) are not very large and the same kind of component control which is exhibited in the other two binaries could be operating in this binary. Although these relationships are interesting, they are not particularly significant in suggesting basic encapsulation mechanisms.

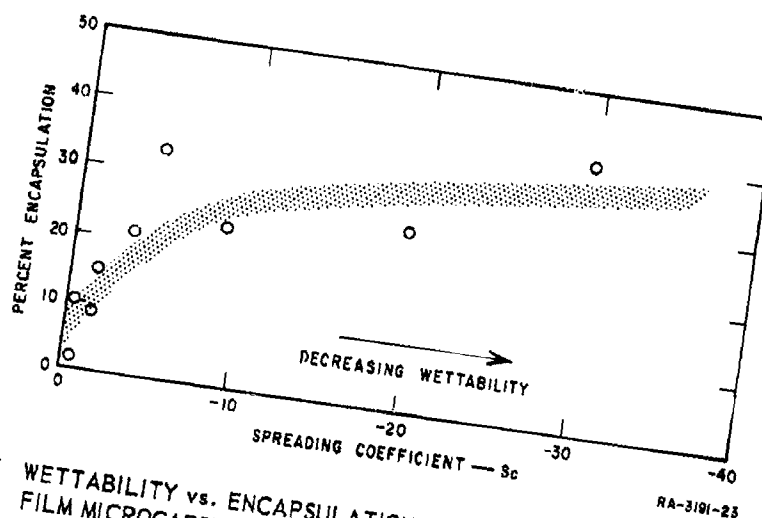


FIG. 7 WETTABILITY vs. ENCAPSULATION EFFICIENCY FOR EVAPORATED FILM MICROCAPSULES

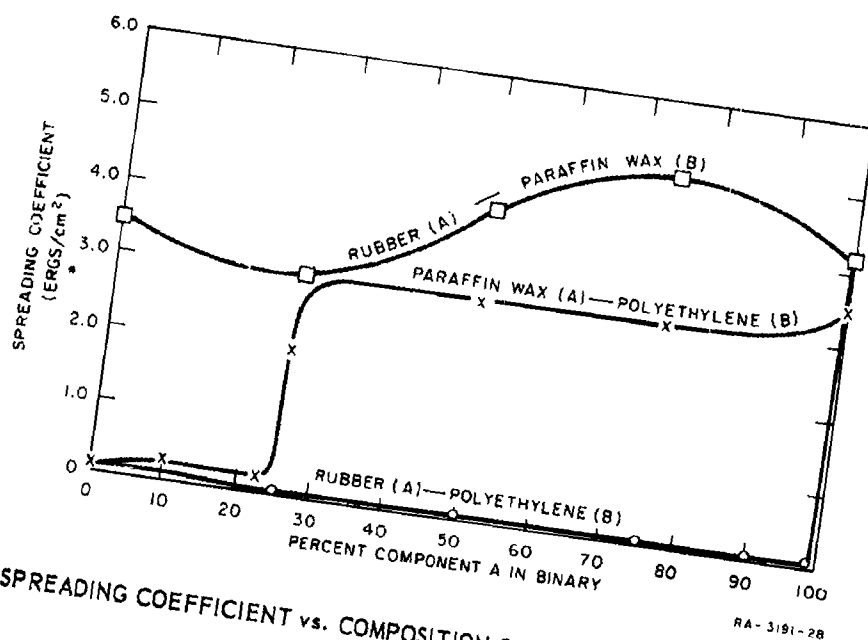


FIG. 8 SPREADING COEFFICIENT vs. COMPOSITION OF SOLID BINARY FILM MATERIAL



Table VII  
PHYSICAL PROPERTIES OF MICROCAPSULE COMPONENTS:  
DIBUTYL PHOSPHITE CORES WITH PARAFFIN WAX AND  
POLYETHYLENE FILMS

| Composition of Solid Film<br>(% of Weight) |              | Spreading<br>Coefficient<br>(ergs/cm <sup>2</sup> ) | Viscosity of<br>Encapsulating<br>Solution<br>(Toluene + Solute)<br>(centipoises at 25°C) | Density of<br>Encapsulating<br>Solution<br>(25°C) | Aerosol<br>Encapsulation<br>Efficiency<br>(Core-DBP)<br>(wt % encapsulated) |
|--|--------------|---|--|---|---|
| Paraffin                                   | Polyethylene |   |  |   |   |
| 100  | 0            | -3.6  | 0.617  | 0.857   | 21  |
| 99   | 1            | -3.3  | 0.622  | 0.857   |   |
| 90   | 10           | -3.1  | 0.610  | 0.858   |   |
| 75   | 25           | -3.2  | 0.603  | 0.859   | 25  |
| 50   | 50           | -3.0  | 0.605  | 0.861   | 25  |
| 25   | 75           | -2.3  | 0.602  | 0.862   | 30  |
| 22.5                                       | 77.5         | -0.23   | 0.604  |   | 10  |
| 20   | 80           | -0.20   |  |   |   |
| 17.5                                       | 82.5         | -0.08   |  |   |   |
| 15   | 85           | -0.10   |  |   |   |
| 12.5                                       | 87.5         | -0.07   |  |   |   |
| 10   | 90           | -0.09   | 0.594  |   |   |
| 1  | 99           | -0.11   |  |   |   |
| 0  | 100          | -0.11   | 0.532  | 0.862   | 11  |

Table VIII  
PHYSICAL PROPERTIES OF MICROCAPSULE COMPONENTS:  
DIBUTYL PHOSPHITE CORES WITH PARAFFIN WAX AND RUBBER IN THE FILMS

| Composition of Solid Film<br>(% of Weight) |        | Spreading<br>Coefficient<br>(erg/cm <sup>2</sup> ) | Viscosity of<br>Encapsulating<br>Solution<br>(Toluene + Solute)<br>(centipoises at 25°C) | Density of<br>Encapsulating<br>Solution<br>(25°C) | Aerosol<br>Encapsulation<br>Efficiency<br>(Core--DBP)<br>(wt % encapsulated) |
|--|--------|--|--|---|--|
| Paraffin                                   | Rubber |  |  |   |  |
| 100  | 0      | -3.6   | 0.417  | 0.857   | 21   |
| 75   | 25     | -3.0   | 0.418  | 0.859   | 25   |
| 50   | 50     | -3.6   | 1.099  | 0.861   | 29   |
| 25   | 75     | -5.0   | 1.323  | 0.863   | 29   |
| 0  | 100    | -4.2   | 1.437  | 0.865   | 33   |

Table IX  
PHYSICAL PROPERTIES OF MICROCAPSULE COMPONENTS:  
DIBUTYL PHOSPHITE CORES WITH POLYETHYLENE AND RUBBER IN THE FILMS

| Composition of Solid Film<br>(% of Weight) |        | Spreading<br>Coefficient<br>(erg/cm <sup>2</sup> ) | Viscosity of<br>Encapsulating<br>Solution<br>(Toluene + Solute)<br>(centipoises at 25°C) | Density of<br>Encapsulating<br>Solution<br>(25°C) | Aerosol<br>Encapsulation<br>Efficiency<br>(Core--DBP)<br>(wt % encapsulated) |
|--|--------|--|--|---|--|
| Poly-<br>ethylene                          | Rubber |  |  |   |  |
| 100  | 0      | -0.11  | 0.532  | 0.862   | 11   |
| 75   | 25     | -0.02  | 0.628  | 0.862   | 38   |
| 50   | 50     | -0.02  | 0.719  | 0.863   | 21   |
| 25   | 75     | -0.05  | 0.876  | 0.864   | 6  |
| 10   | 90     | -0.16  | 1.115  | 0.864   | 9  |
| 1  | 99     | -0.50  | 1.311  | 0.865   | 30   |
| 0  | 100    | -4.2   | 1.417  | 0.865   | 33   |

In all three systems the viscosities of the film binary solutions in toluene did not depart too greatly from ideal.

It was not possible to bridge the gap between spreading coefficient measurements (liquid core-solid film) and liquid-liquid interfacial tension measurements (liquid core-film solution) with the systems having DBP for the core liquid because the miscibility of DBP and toluene did not permit the existence of a liquid-liquid interface in these systems.

It became obvious that any additional surface information must come from the extrapolation of information from similar systems in which both the core-encapsulating film and the core-film solution interfacial tension measurements can be made.

The spreading coefficient measurements for the films from toluene solution on phosphoric acid cores had already been made. Liquid-liquid interfacial tension measurements were made on the three toluene solution-phosphoric acid pairs by a "drop volume" method. The experimental details of this method are given in the Appendix.

Phosphoric acid was also encapsulated in paraffin oil (white mineral oil with a viscosity of 69 centipoises at 25°C) and the liquid-liquid interfacial tension determined. The interfacial tension and encapsulation data for these four systems are given in Table X.

Next, a solid core-polymer film series was incorporated into the scheme using the same three toluene solutions and oxalic acid. The oxalic acid was dissolved in absolute alcohol (10% by weight-solution) and this solution was used in the generator's first stage. Spreading coefficients of the toluene solutions on oxalic acid were determined and these data are presented in Table XI.

In the phosphoric acid-solid film series, as in the more important DBP-solid film series, the encapsulation efficiency increases with decreasing wettability of the film by the core liquid. If we consider the

Table X

LIQUID-LIQUID INTERFACIAL TENSIONS

| Film Type                           |  | Liquid-Liquid<br>Interfacial<br>Tension at 25°C<br>(dynes/cm) | Aerosol Encapsulation<br>Efficiency<br>(Core--Phosphoric Acid)<br>(wt % encapsulated) |
|-------------------------------------|--|---|---|
| Solid Film from<br>Toluene Solution | Liquid Film                            |   |   |
| Paraffin wax                        |  | 27  | 26  |
| Polyethylene                        |  | 26  | 14  |
| Rubber                              |  | 11  | 39  |
|                                     | Paraffin oil<br>(white mineral<br>oil) | 60  | 26  |

Table XI

SPREADING COEFFICIENT VS ENCAPSULATION  
EFFICIENCY: FILM SOLUTION AND SOLID CORE

| Coating Material | Film Solution in Toluene--<br>Oxalic Acid | Aerosol Encapsulation<br>Efficiency<br>(Core--Phosphoric Acid)<br>(wt % encapsulated) |
|------------------|---|---|
| Paraffin         | -0.17                                     | 24  |
| Polyethylene     | -0.06                                     | 28  |
| Rubber           | -0.09                                     | 61  |

liquid-liquid interfacial tension between the phosphoric acid core and the toluene solutions instead, the encapsulation efficiency (i.e., weight fraction phosphoric acid encapsulated) may be seen to be a direct function of the product of the concentration of the solution and the reciprocal of the interfacial tension. The reciprocal of the interfacial tension may be considered to be the mutual "wettability" between the two liquids. The paraffin oil on phosphoric acid shows the same relationship.

Now, if we consider the film solutions encapsulating solid oxalic acid cores, we arrive at the same kind of relationship. The encapsulation efficiency of the polymer films on the solid cores is proportional to the product of film solution concentration, and the negative reciprocal of the spreading coefficient. (Again, the negative reciprocal of the spreading coefficient is wettability.)

Thus the factors controlling encapsulation in the simpler systems exhibit an internal consistency. Also, all of the liquid core-film solution systems exhibit an internally consistent relationship between encapsulation efficiency and spreading coefficient of the core liquid on the solid. From the above, it may be inferred that the factors controlling encapsulation in the simpler systems are the real controlling factors in the systems composed of hydrophobic liquid cores and polymer coats; and furthermore those indirect properties which are measurable, are related to the controlling properties and are therefore of value in characterizing microcapsule pairs.

## XI COMPREHENSIVE TABLE - PREPARATION AND PROPERTIES OF ENCAPSULATED AEROSOLS

During the course of this work a number of techniques for the production of encapsulated aerosols have been investigated. These methods included those previously developed or suggested, plus new approaches. A summary of the information covering all of these methods concerning generation details, kinds of encapsulated aerosols possible, particle size ranges, encapsulation efficiencies, and other pertinent data is presented in Table XII.

Tabl XIII  
PREPARATION AND PROPERTIES OF ENCAPSULATED AEROSOLS\*

|  | Direct Methods of Generation Involving Condensation<br>(Microcapsules Formed in Aerosol)   |  |  | Direct Methods of Generation Involving Completion<br>(Microcapsules Formed on Mixing of Two Aerosols)      |   | Indirect Methods of Generation<br>(Microcapsules Must Be Redispersed)   |   |  |
|--|--|--|--|--|---|---|---|--|
|  | Simple Physical Condensation   | Condensation-Polymerization of Vapor Phase Monomer                           | Condensation Followed by Liquid Phase Polymerization                     | Inertial Two-Stage Aspirator Generator   | Electrostatic   | Liquid Phase Concentration Plus Spray Drying  | Spray Drying of Two Phase Suspension or Emulsion          | Inertial Inspection in Fluid Energy Mill   |
| Typical microcapsules  | Tetracycline phosphate in lauric acid-tricresyl phosphate in ammonium chloride   | Phosphoric acid in polymerized isoprene gum (gaseous $\text{NO}_2$ catalyst) | Phosphoric acid in polymerized tung oil (gaseous $\text{NO}_2$ catalyst) | Dibutyl phosphite in polyethylene  | Glass in phosphoric acid  | Dibutyl phosphite in polyvinyl formal, dibutyl phthalate in gelatin   | Dibutyl phosphite in polyethylene                         | Oxalic acid in mineral oil   |
| Kinds of microcapsules   | All four phase combinations of microcapsules feasible. Possibilities limited by thermal stability, chemical propa. and proper volatility of components | Many different core materials may be encapsulated                            | Core material must be thermally stable                                   | Many combinations of liquid core and solid polymer coat in a solution                                      | Any liquid on solid combination. Both components must be predisposed as aerosols  | Practically confined to solid-on-liquid pairs of proper solubility relationship for concentration (hydrophilic core or reverse) | Solid-on-liquid or solid-on-solid pairs must be insoluble | Many liquid-on-solid and liquid-on-liquid pairs. Solubility relationship not important |
| Highest temperature during generation                          | 160°C  | Room temperature   | 200°C  | Room temperature. Second stage may be heated to use low melting point solids for encapsulation in solvents | Room temperature. Electric field corona discharge, one positive corona at 9 kv, one negative corona (glass aerosol) at 5 kv | 35°C  | 35°C  | Room temperature   |
| Encapsulation efficiency (wt. % of core material encapsulated) | Good > 90%   | Fair to good. Up to 90%  | Fair. Up to 60%  | Fair to good. Up to 90%  | Excellent. 100%   | Excellent. Usually 100%   | Very good. Up to 100%                                     | Very good. Up to 100%  |
| Particle size range  | 6-9 $\mu$<br>1.2/1   | 2-20 $\mu$<br>~ 1/1  | 9-40 $\mu$<br>~ 4/1  | 3-15 $\mu$<br>~ 1/1  | 10-50 $\mu$<br>< 1/1  | 2-10 $\mu$<br>1/1   | 2-12 $\mu$<br>1/1   | 2-5 $\mu$<br>3/1   |
| Minimum practical coat/core weight ratio                       | Good   | Fair   | Not known  | Good. Cores must be protected from water vapor   | Poor  | Good. Cores must be protected from water vapor  | Good. Cores must be protected from water vapor            | Poor   |
| Storage stability  | Good   | Preliminary procedure evolved  | Preliminary procedure evolved  | Used to produce a large number of encapsulated aerosols  | Satisfactory procedure has been evolved   | Well developed. Many patents issued   | Simple technique. Good where applicable                   | Little development to date   |
| Present state of development                                   | Procedures developed for six encapsulated aerosols   |  |  |  |   |   |   |  |

\* Specific information refers to the types of encapsulated aerosols studied to date.

## XII CONCLUSIONS

Aerosols may be encapsulated by "polymerization-condensation" of gaseous monomers, using a gaseous promoter or catalyst. These generation methods have possible application outside the laboratory inasmuch as the reaction volumes in the aerosol need not be excessive.

A two-stage aspirator generator can successfully generate many liquid-core-polymer film encapsulated aerosols. Proper polymer solvent and optimum solution concentration in the second stage of the generator generally lead to satisfactory microencapsulation.

The fluid energy mill can be used to produce encapsulated aerosols by closing the collecting cyclone. This device lends itself best to the generation of liquid-on-solid microcapsules.

Wettability appears to be the most important property controlling microencapsulation. Encapsulation efficiency increases with wettability. Viscosity of liquid components is not an important encapsulation property. The important class of encapsulated aerosols, hydrophobic liquid cores with polymer films, because of the miscibility of the core liquid with the polymer solvent, cannot be characterized directly as to the effect of wettability. However, the encapsulation efficiency of these systems is tied to the artificial parameter, wettability of the solid film by the core liquid. In all liquid core-film solution systems the encapsulation efficiency was found to be inversely proportional to the wettability of the solid film by the core liquid.

The mechanism involved in the process of microencapsulation remain only partially understood. Further investigation of the possible roles of other interface-related properties should be valuable. Also, much more work should be done concerning the effects of microencapsulation on the behavior of aerosol systems.



### XIII CONTRIBUTING PERSONNEL

Persons who contributed to the project were Dr. R. D. Cadle, Chairman, Atmospheric Chemical Physics Department, Mr. C. E. Lapple, Senior Scientist, Dr. Zoila Reyes, Senior Organic Chemist, Dr. R. C. Robbins, Physical Chemist, and Mrs. Jill Thomas, Chemist.



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Robert C. Robbins, Physical Chemist  
Atmospheric Chemical Physics Department

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## APPENDIX

### A. The Measurement of Drop Height

The measurements were made with a spherometer which was rigidly mounted on a horizontal glass stage. The apparatus is schematically presented in Fig. 9. The solid films were laid down on glass microscope slides which were positioned on the stage.

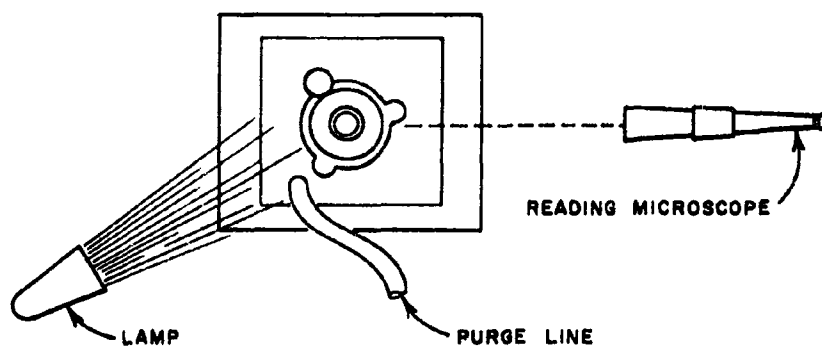
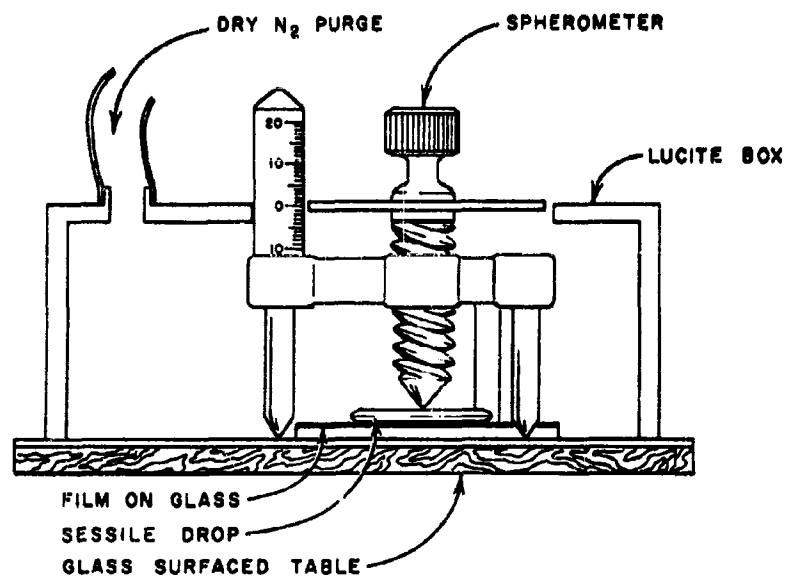
A standard technique was developed for placing the liquid drop on the solid film. The liquid was fed from a syringe in the form of a doughnut with the last of the liquid added to the hole. This technique assured a sufficiently large drop radius to establish equilibrium conditions with the drop height independent of drop size.

Immediately after placing the liquid drop, a plastic box with a gas line attached was put in place over the slide and a dry nitrogen purge was started. A 100-watt protection lamp was used to illuminate the film and the drop. The exact vertical position of the spherometer point was observed by means of the measuring microscope, making it easy to position the point of soft film or liquid drop surfaces with an accuracy of  $\pm 10 \mu$ . Drop height was taken as the difference between the readings at the middle of the top surface of the drop and the top surface of the film on which the drop rested.

The method is capable of determining spreading coefficients as small as  $-0.05 \text{ erg/cm}^2$  with an accuracy of  $\pm 0.01 \text{ erg/cm}^2$ .

### B. Interfacial Tension by a Drop-Volume Method

The drop-volume method for the measurement of liquid-liquid interfacial tension was selected as the best general method for accuracy, speed, and over-all convenience. An example of one of the apparatus configurations is shown in Fig. 10. The liquid in the syringe and capillary must be the poorer glass wetter to obtain correct measurements. In the



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FIG. 9 APPARATUS FOR MEASURING SPREADING COEFFICIENT

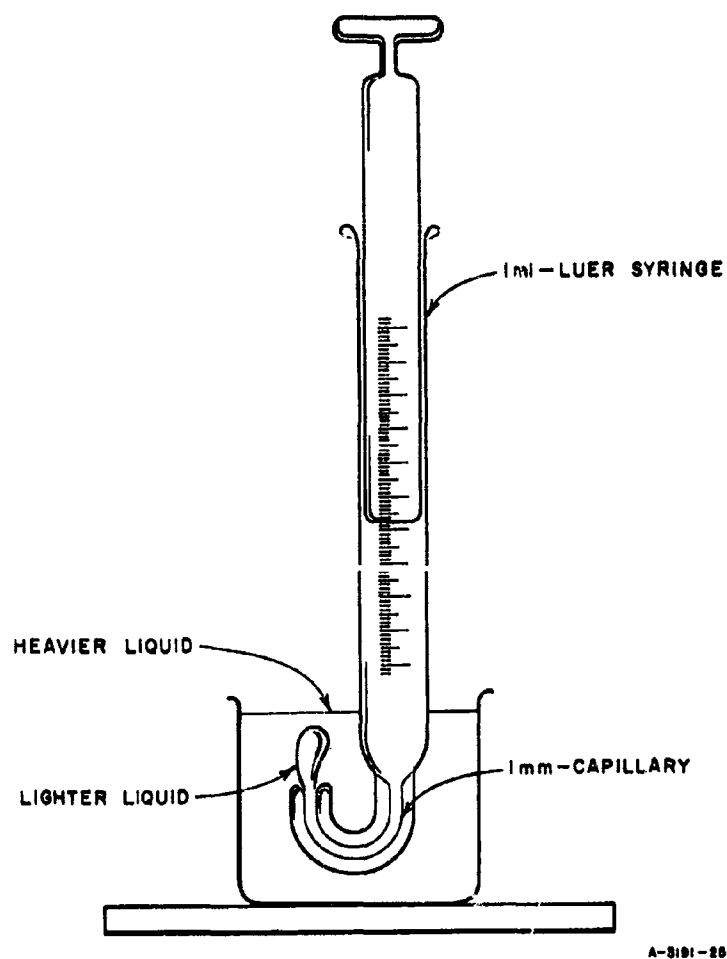


FIG. 10 APPARATUS FOR MEASURING INTERFACIAL TENSION

illustrated example the poor glass wetter is the lighter liquid. Straight capillary tips were used for introducing drops of the heavier liquid of a pair when it was the poorer glass wetter. The capillary tip was immersed in the other liquid of the liquid pair and the syringe clamped in place. Several drops were pushed out the capillary tip by slowly depressing the syringe barrel. By displacing nearly one milliliter of liquid and counting the drops, the average drop volume was estimated to  $\pm 1$  microliter. Measurements were made at  $25 \pm 0.5^\circ\text{C}$ .

The interfacial tension was calculated from the expression:

$$\gamma_{ab} = [V(\rho_b - \rho_a)g/r] \cdot F$$

where  $\gamma_{ab}$  is the interfacial tension between liquids a and b, V is the volume of one drop,  $\rho_a$  and  $\rho_b$  are the densities of the lighter liquid and the heavier liquid, respectively, g is the gravitational constant, r is the inside tip radius, and F is a factor which corrects for the departure of the drop radius from r and is a function of the ratio  $r/V^{1/3}$ . The F values, taken from the International Critical Tables, Vol. IV are:

| $r/V^{1/3}$ | F     |
|-------------|-------|
| 0.0385      | 0.172 |
| 0.159       | 0.198 |
| 0.258       | 0.215 |
| 0.344       | 0.266 |
| 0.383       | 0.230 |
| 0.422       | 0.235 |
| 0.459       | 0.240 |
| 0.495       | 0.244 |
| 0.529       | 0.248 |
| 0.599       | 0.254 |
| 0.662       | 0.259 |
| 0.725       | 0.262 |
| 0.781       | 0.265 |
| 1.01        | 0.260 |
| 1.07        | 0.255 |
| 1.17        | 0.246 |

Interfacial tension values of two standard liquid pairs were measured. These and values from the International Critical Tables (ICT) are listed below.

| <u>System</u>             | <u>Exp. <math>\gamma</math></u> | <u>Lit. <math>\gamma</math> (ICT)</u> |
|---------------------------|---------------------------------|---------------------------------------|
| Water-benzene             | $35 \pm 2$                      | $35.00 \pm 0.05$                      |
| Water-carbontetrachloride | $42 \pm 2$                      | $45.0 \pm 1.0$                        |

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